SOME COMMENTS ON THE BUERGER PRECESSION METHOD FOR THE DETERMINATION OF UNIT CELL CONSTANTS AND SPACE GROUPS

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ABSTRACT

Some comments on the effectiveness of the Buerger precession method and the method of de Jong and Bouman for unit cell and space group studies are made and certain practical advantages of the former are pointed out. A test of the accuracy of unit cell dimensions based on measurement of precession films is described. The effect of decreasing precession angles for upper levels in shortening exposure times is illustrated.

SOME COMMENTS ON THE BUERGER PRECESSION CAMERA

The Buerger precession method (1, 2), like the method of de Jong and Bouman (3), gives enlarged, undistorted pictures of the central areas of the reciprocal lattice of a crystal. The spacings of the rows of points and the interaxial angles of the plane level nets are obtained directly by measurements on the films themselves and are converted readily into axial translations and interaxial angles in direct space. Simple inspection of the plane nets of zero level photographs and comparison with those of upper levels is all that is required to establish the diffraction symbol of the crystal; no tedious indexing, plotting, or reconstruction of the reciprocal lattice is required. For purposes of detailed structure investigations, both methods, of course, suffer from the fact that the back-reflection range is not covered. For the establishment of space groups and the determination of unit cell constants to an ordinarily acceptable degree of accuracy, however, the Buerger precession camera and the de Jong-Bouman instrument are ideally suited; in certain respects, such as speed and absence of ambiguity, they are superior to other methods.

Although both de Jong-Bouman and Buerger precession films share the same desirable feature of undistorted reproduction of reciprocal lattice levels, the precession camera has certain advantages in practice. One of these is due to the relationship between the rotation axis of the goniometer head and the crystal axis normal to the reciprocal lattice level to be photographed. In the de Jong-Bouman instrument, as in simple rotating crystal and in Weissenberg cameras, the two coincide whereas they are at right angles to each other in the precession instrument. Thus in the de Jong-Bouman method the crystal must be reoriented (which usually involves remounting) on the goniometer head for a survey of the reciprocal lattice levels normal to a second crystallographic axis. Thus at least two mountings and orientations of a given crystal usually are required for a complete unit cell and space group study. If the crystal lacks suitable faces for use on a two-circle reflecting goniometer, as in the case of a broken fragment, this may be very time-consuming and, in extreme cases, become a frustrating "trial and error" procedure. With the precession instrument, however, the precession axis is at right angles to that axis of the goniometer head which coincides with the rotation axis in other instruments and provision is made for locking the crystal in any angular position around this axis of the goniometer head. Levels normal to two precession axes, therefore, can be examined without remounting the crystal. This is particularly valuable in the case of crystals belonging to the cubic, tetragonal, orthorhombic, monoclinic, and hexagonal systems. Furthermore, as Professor Buerger has pointed out (2), if a small precession angle is employed, preferably without filter or layer-line screen, even the single orientation normally required can be effected solely by precession photographs.

Another useful consequence of the fact that the precession axis is at right angles to the axis of the goniometer head is that, with the usual precession angle of 20°, the axis of the goniometer head during precession makes a minimum angle of 70° with that of the pin-hole system. Thus there is ample clearance for the usual type of precision goniometer head with screw-adjustable arcs and lateral translations. On the other hand, this angle is reduced to 45° for the zero level in the most useful form of the de Jong-Bouman method (equal-cone with cone angle of 45°) which does not permit use of the usual size head with graduated arcs. Less bulky devices in which a ball-and-socket joint replaces the arcs and a sliding plane replaces the sledge motions (1, p. 184) can be employed, but only if accurate orientation of the crystal is possible by optical methods. The difficulty disappears for upper levels because the angle between the axis of the goniometer head (rotation axis) and that of the pin-hole system increases for constant cone angle and increasing height of level. Selection of a smaller cone angle to permit use of the larger head for the zero level, however, causes a rapid increase in the circular blank area in the center of the photographs of the first few upper levels (maximum when the height of the level equals the sine of the cone angle) and these are the ones that require shorter exposure times and hence are the most desirable to use.

Finally, it may be noted that exposure times for a specific reciprocal lattice level of a given crystal generally are longer with the de Jong-Bouman than they are with the precession camera.

The Accuracy of the Precession Method

On several occasions doubts have been expressed regarding the accuracy with which unit cell dimensions can be obtained from measurements of precession films as compared with other types such as Weissenberg photographs. Detailed data given in a recent communication (4) on the determination of the unit cell constants of probertite show that zero level photographs obtained with the rigid zero level cassette of the precession camera warrant use of the special measuring device developed by

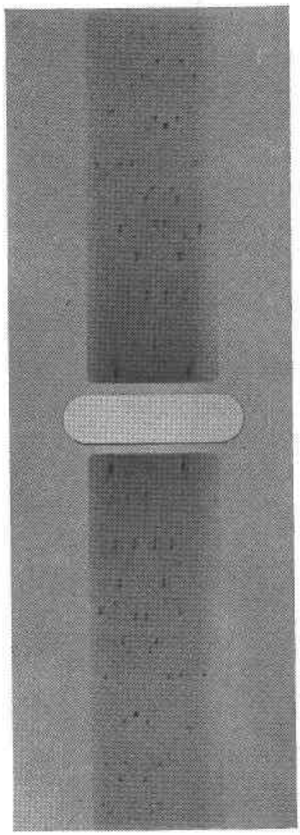

FIG. 1. Precision back-reflection Weissenberg photograph of lindgrenite. (Reflections from (010) lie on the central (symmetry) line).

Professor Buerger (5) that enables linear measurements to be made to 0.05 mm. and angular measurements to 5 minutes of arc. Results obtained during a recent investigation (6) of the unit cell dimensions of lindgrenite indicate a reproducibility of such constants to better than 0.2% or 0.3%, which compares favourably with other methods other than those designed specifically for very high precision.

As a test of the absolute accuracy of the precession method the length of the b axis of lindgrenite was determined with Professor M. J. Buerger's precision back-reflection Weissenberg camera (1, chap. 21). A previous study (6) by the precession method had given 14.03 Å and 14.07 Å for this translation from two sets of films from separate crystals. Preliminary calculations for a large number of possible target materials showed that spots due to nine reflections ($n\lambda = 20\beta_1$, $18\alpha_2$, $18\alpha_1$, $18\beta_1$, $16\alpha_2$, $16\alpha_1$, $16\beta_1$, $14\alpha_2$, $14\alpha_1$) from (010) were potentially recordable within the limited range of the precision Weissenberg using unfiltered copper radiation. Two photographs of the same crystal were obtained using a modified Hadding gas tube and a Philips diffraction unit, respectively. They will be referred to as film 1 and film 2. The latter is reproduced in Fig. 1 and it will be observed that the shapes of the spots are not ideal for maximum precision of measurement. They are due to the tabular shape of the crystal fragment resulting from the fact that lindgrenite has perfect (010) cleavage. The films are sufficiently good, however, for the present purpose. The separation (F) of equivalent spots along a direction normal to the center line of the photographs was measured to 0.05 mm. Computations were made as described by Buerger (1, chap. 21) and based on the relations $d = (n\lambda/2)/\cos(F/4)$ and $\sin^2(90° - \theta) = \sin^2(F/4)$. The following values (7) for λ were employed: $CuK\alpha_2$, 1.54434 Å; $CuK\alpha_1$, 1.54050 Å; $CuK\beta_1$, 1.39217 Å. Results are shown in Table 1.

TABLE 1

Cu $n\lambda$	Film 1			Film 2		
	F(mm.)	d(Å)	$\sin^2(90°-\theta)$	F(mm.)	d(Å)	$\sin^2(90°-\theta)$
$20\beta_1$	28.45	14.0298	0.015349	28.72	14.0317	0.015622
$18\alpha_2$		(absent)		31.52	14.0316	0.018796
$18\alpha_1$	35.30	14.0309	0.023581	35.32	14.0308	0.023563
$18\beta_1$		(absent)			(absent)	
$16\alpha_2$	113.00	14.0253	0.22403	113.07	14.0276	0.22429
$16\alpha_1$	114.10	14.0278	0.22817	114.07	14.0257	0.22793
$16\beta_1$	149.65	14.0227	0.36919	149.82	14.0299	0.36983
$14\alpha_2$	158.35	14.0267	0.40602	158.27	14.0235	0.40575
$14\alpha_1$	158.95	14.0223	0.40860	158.88	14.0196	0.40837

It will be observed that the spot due to $18\beta_1$ was not recorded on either film and that the one due to $18\alpha_2$ appeared only on film 2 which was given a longer exposure than film 1. The results tabulated for film 2 are the averages for three measurements made at different times. Corresponding values of F for the two films are in good agreement except for the spots due to $20\beta_1$ and $16\beta_1$. The difference (0.27 mm.) in the case of the $20\beta_1$

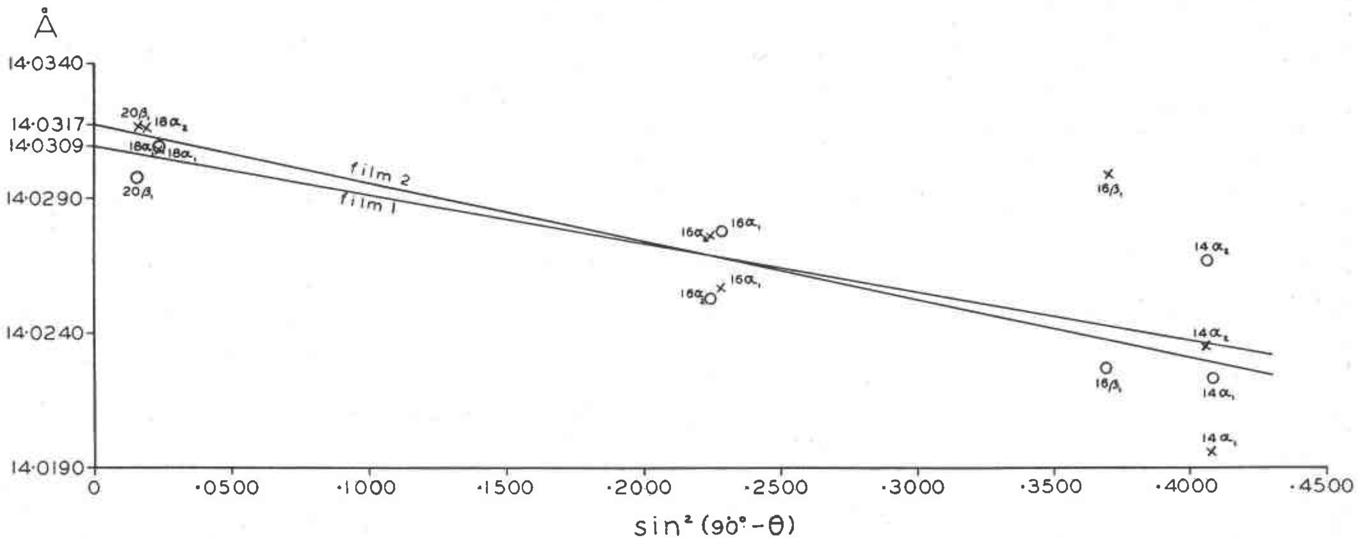

FIG. 2. Bradley-Jay plot of $d_{(010)}$ (b) against $\sin^2(90°-\theta)$ for lindgrenite extrapolated to $\sin^2(90°-\theta)=0$.

spots is serious from the point of view of very high precision because points in this region, where $\sin^2 (90° - \theta)$ approaches zero, have the greatest weight in determining the final value of d. For this reason, data for the two films have been plotted separately in Fig. 2, those for film 1 being represented by circles and those for film 2 by crosses. The scatter of points at higher values of $\sin^2 (90° - \theta)$ is not as serious as it appears on the scale to which Fig. 2 has been drawn. For example, in the region of $\sin^2 (90° - \theta) = 0.408$ an error of 0.10 mm. in F leads to a difference of about 0.005 Å in the value of d and F is the difference between two measurements each of which is made only to the nearest 0.05 mm. In view of these factors, and particularly the discrepancy in the values for $20\beta_1$, the results for d at $\sin^2 (90° - \theta) = 0$, namely, 14.0309 Å and 14.0317 Å, are in reasonable agreement. The average, $d = 14.031$ Å, probably is accurate to one or two units in the third decimal place. It certainly justifies the assumption that the absolute accuracy of results obtained by the precession method is as good as their reproducibility, namely, 0.2% to 0.3% or better.

The Effect on Exposure Time of Decreasing the Precession Angle

Precession photographs of a given crystal require much shorter exposures than do Weissenberg photographs of the same level and they can be reduced still further by decreasing the precession angle. For the zero level it is desirable to record as much of the net as the 5″×5″ film will permit because measurements of row spacings and interaxial angles are best carried out on these pictures. The useful range of crystal-to-film distance (i.e., the magnification factor, F) is about 4.50 cm. to 7.50 cm. so that 6.00 cm. is a convenient setting; with this distance a precession angle of 20° is very satisfactory. Exposure times in general increase for upper levels and, if the precession angle remains constant, an unrecordably large area of the reciprocal lattice level may cut through the sphere of reflection during precession. The exposure time, therefore, can profitably be reduced by decreasing the angle of precession. Unfortunately in upper level photographs the effect of decreasing the precession angle is to increase the blank area in the center of the film as in the case of de Jong-Bouman photographs mentioned previously. However, for the purposes of a space group investigation this does not matter providing that the remaining annular record is broad enough to show the main features of the net. For example, Figs. 3 and 4 are precession photographs of the b-axis first level of childrenite obtained with Mo radiation (zirconium oxide filter). A precession angle of 20° was used for Fig. 3 and an exposure time of 3.5 hours whereas with a precession angle of 6°50′ (corresponding to a cone angle of 20° between the precession axis and the diffracted rays) a some-

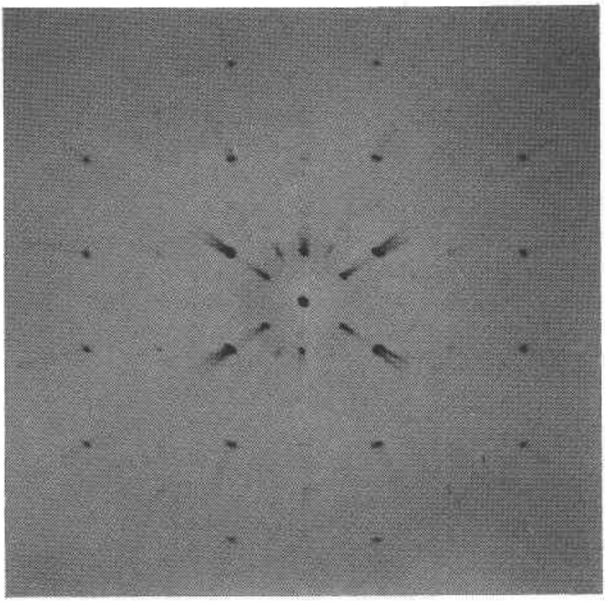

FIG. 3. b axis, first level, precession photograph of childrenite, Mo radiation, $\bar{\mu}=20°$, exposure 3.5 hrs.

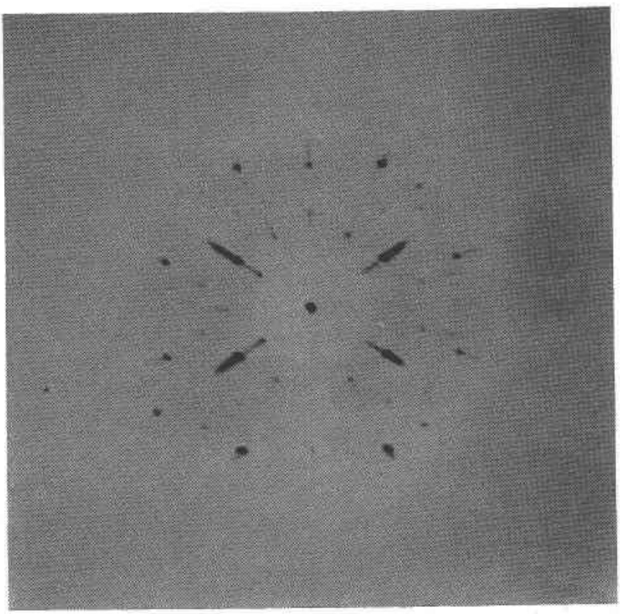

FIG. 4. b axis, first level, precession photograph of childrenite, Mo radiation, $\bar{\mu}=6°50'$, exposure 2.5 hrs.

what more dense photograph (Fig. 4) was obtained in 2.5 hours. As will be observed, the annular area of the plane net recorded in Fig. 4 is more than adequate for recognition of its main features, namely, diamond with the center of the net at a diamond corner (8).

Acknowledgments

I am deeply indebted to Professor M. J. Buerger for his courtesy in placing his unique collection of moving-film equipment at my disposal. Grateful acknowledgment also is made to the John Simon Guggenheim Memorial Foundation for a Fellowship and to McGill University, Montreal, for leave-of-absence which made an extended visit to the Massachusetts Institute of Technology possible.

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